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# OPTIMIZATION OF MINUTE DOPING OF $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ THIN FILMS WITH RE = Tb AND Nd (POSTPRINT)

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Doping of $YBa_2Cu_3O_{7-\delta}$ (YBCO) has become an effective means of increasing the flux pinning and critical current densities ($J_c$) in thin film superconductors, while maintaining the transition temperature ($T_c$). In previous research efforts, our group showed that doping ($Y_{1-x}RE_x$)BCO with typically deleterious rare earth (RE) elements can be used to improve the film's current density via flux pinning when the x molar additions are less than 1%. However, data was only presented for different orders of magnitude (x = 0.1%, 1.0%, 10%) without consideration of optimization. The research presented here demonstrates that the deleterious RE elements can differ greatly in how broad the range of optimal doping concentration is, in addition to the relative doping concentration. Rare-earth elements Nd and Tb were compared due to the difference in degradation mechanisms: Nd additions results in Ba site substitution and Tb123 exhibits poor phase formation. Thin films of Nd and Tb doped YBCO films were grown by pulsed laser deposition (PLD) using standard deposition parameters for plain YBCO. The compositions studied were ($Y_{1-x}RE_x$)BCO where x was varied from 0.0001 to 0.025 for Nd and 0.005 to 0.015 for Tb. Targets for PLD were prepared using solid state reaction and sintering procedures. All films were characterized for $J_c$ and $T_c$ by vibrating sample magnetometry. Data for $J_c$(H,T) and $T_c$ were compared to undoped YBCO films processed under the same conditions. The results show a measurable increase in flux pinning for both different concentrations and range of Nd and Tb doping, with little decrease in $T_c$.

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# Optimization of minute doping of $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$ thin films with RE = Tb and Nd

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## ABSTRACT

Doping of $YBa_2Cu_3O_{7-\delta}$ (YBCO) has become an effective means of increasing the flux pinning and critical current densities ($J_c$) in thin film superconductors, while maintaining the transition temperature ($T_c$). In previous research efforts, our group showed that doping ($Y_{1-x}RE_x$)BCO with typically deleterious rare earth (RE) elements can be used to improve the film's current density via flux pinning when the x molar additions are less than 1%. However, data was only presented for different orders of magnitude (x = 0.1%, 1.0%, 10%) without consideration of optimization. The research presented here demonstrates that the deleterious RE elements can differ greatly in how broad the range of optimal doping concentration is, in addition to the relative doping concentration. Rare-earth elements Nd and Tb were compared due to the difference in degradation mechanisms: Nd additions results in Ba site substitution and Tb123 exhibits poor phase formation. Thin films of Nd and Tb doped YBCO films were grown by pulsed laser deposition (PLD) using standard deposition parameters for plain YBCO. The compositions studied were ($Y_{1-x}RE_x$)BCO where x was varied from 0.0001 to 0.025 for Nd and 0.005 to 0.015 for Tb. Targets for PLD were prepared using solid state reaction and sintering procedures. All films were characterized for $J_c$ and $T_c$ by vibrating sample magnetometry. Data for $J_c$(H,T) and $T_c$ were compared to undoped YBCO films processed under the same conditions. The results show a measurable increase in flux pinning for both different concentrations and range of Nd and Tb doping, with little decrease in $T_c$.

## INTRODUCTION

Many methods are being considered worldwide to enhance the current carrying properties of $YBa_2Cu_3O_7$ (YBCO) coated conductors in applied magnetic fields, by adding defects of many sizes, phases and orientations [1-3]. These defects act as flux pinning centers, which trap the quantized magnetic vortices in the crystal lattice that penetrate the type-II superconductor, allowing a greater supercurrent to flow without dissipation. In previous work, it was shown that doping ($Y_{1-x}RE_x$)BCO with typically deleterious rare earth (RE) elements can be used to improve the film's current density via flux pinning when the x molar additions are less than 1% [4-5]. In the case of these minute dopants, defects are added to YBCO by considering substitution of the Y element with a deleterious RE element that characteristically result in locally depressed superconducting properties. However, data was only presented for different orders of magnitude (x = 0.1%, 1.0%, 10%) without consideration of optimization.

It is important to understand how the deleterious RE elements can differ with respect to how broad the range of optimal doping concentration is, in addition to the relative doping concentration. A smaller step size in dopant quantities will help determine the range of optimal doping. Another critical factor to understand is whether the pinning properties created by this

method either behave similarly or differently for the various deleterious dopants, especially since the degradation phases formed or pinning mechanisms of the different minute dopants can differ.

For this study we choose to more fully observe the effects of doping with Nd and Tb in minute concentrations. While many RE elements have been considered for substitution in $(Y_{1-x}RE_x)BCO$, neither RE = Nd nor Tb have been considered in typical amounts of 10-40 % due to their deleterious effects. These dopants were specifically chosen for their different interactions with YBCO. Additions of Nd in YBCO are typically detrimental due to site substitution with the Ba as opposed to the Y due to its atomic size [6]. Additions of Tb tend to be detrimental since Tb-Ba-Cu-O does not readily form a superconducting $TbBa_2Cu_3O_7$ phase [7]. In either case, non-superconducting phases are expected to be formed which would act as flux pinning centers, especially if their size is greater than the YBCO coherence length = 3-4 nm at 65-77 K. Cross-sectional TEM analysis should reveal how Tb and Nd is interacting in the YBCO. Using the dopants Nd and Tb we find the optimal range of doping YBCO to give the best critical current density ($J_c$) values when a magnetic field is applied to the sample.

## EXPERIMENTAL

Thin films of $(Y_{1-x}RE_x)BCO$ were grown by pulsed laser deposition (PLD). A Lambda Physik LPX 300 KrF excimer laser ($\lambda$ = 248nm) was used, with spot size ~ 1.0x0.13$cm^2$ and fluence of ~ 3 J/$cm^2$. The depositions were completed at 790°C with a background pressure of 300 mTorr $O_2$ [8], and films were annealed after deposition at 500°C for 30 minutes in one atmosphere of 99.999% pure $O_2$. The film deposition rate was ~15 nm/minute, or equivalently 2.5 Å/s, and film thickness was kept in the range of 250-300 nm. Lanthanum aluminate (LAO) single crystal substrates were used for films, having dimensions of 3.2x3.2x0.5$mm^3$ and 4 x 10x0.5$mm^3$. The substrates were ultrasonically cleaned with acetone and isopropyl alcohol for five minutes in each solvent. Once clean, the substrates were affixed directly to a YBCO coated heater block by means of colloidal silver paint. These deposition parameters are those typically used to deposit plain YBCO [8], and additional optimization of the parameters was not necessary for the minutely doped samples.

Targets of $(Y_{1-x}RE_x)BCO$ with RE = Nd or Tb were mixed, pressed and sintered using commercially available powders by solid state reaction techniques. The Tb doped targets were prepared using precursor powders of $Y_2O_3$, $BaCO_3$, CuO, and $Tb_4O_7$ to form $Y_{1-x}Tb_xBa_2Cu_3O_7$ (YTBCO) as described by Kell et al. [4] where x = 0.005, 0.01, and 0.015. The Nd doped targets were prepared from precursor powders of YBCO (Nexans Powder) and $NdBa_2Cu_3O_7$ (NdBCO) (99.9% purity) where x= 0.0001, 0.0005, 0.001, 0.005, 0.0075, 0.015 and 0.025. The precursor powders were first dried at 450°C for 8 hours in alumina crucibles. YBCO and NdBCO were measured for the needed molar amount of Nd powder and then were mixed in an agate mortar until a homogeneous mixture was formed. The targets were then reacted in air at 850°C for 72 hours and 920°C for 108-168 hours. All targets obtained a density of $\geq$ 90% of theoretical density of pure YBCO.

The magnetic $J_c$ and critical transition temperature ($T_c$) were measured using a Quantum Design Physical Properties Measurement System (PPMS) with a vibrating sample magnetometer (VSM) attachment. Each sample was characterized using the VSM at 77 K and 65 K in a magnetic field of 0 to 9 T. The magnetic data was then used to calculate the magnetic $J_c$ and pinning force ($F_p$) data using a simplified bean model as described by Kell et al. [4]. The $T_c$ was measured using a DC magnetization technique. The films surface morphology was observed using a FEI Sirion scanning electron microscope in ultra high resolution mode at 5 kV.

Microstructure characterization was performed using a JEM-2100 LaB6 transmission electron microscope (TEM).

## DISCUSSION

The measured $T_c$ of the films was slightly depressed as compared to the YBCO thin films. Typical YBCO films had $T_c$s of 90K to 90.5K, and the Nd doped films had a range from 88.5 K to 89 K, while the Tb doped films had a range of 89 K to 90 K. Typically, slight depression in $T_c$ is common when non-superconducting secondary phases are used as pinning centers. Figure 1 shows the pinning force ($F_p$) versus magnetic field plots for 77 K and 65 K for Tb doping. The $F_p$ plots reveal that $(Y_{1-x}Tb_x)BCO$ optimizes over a range of 1%. The $F_p$ peak performance of 1% Tb is ~1.5x's higher pinning than YBCO at its pinning force maximum for 77 K and ~1.8x's higher pinning at 65 K than YBCO.

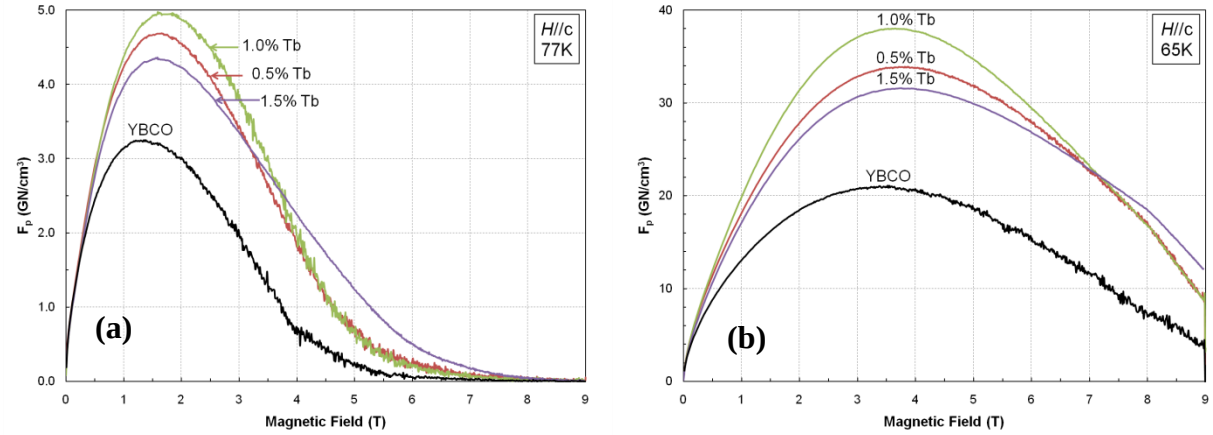


**Figure 1.** (a): Pinning force for Terbium doped films at 77 K, (b): pinning force for Terbium doped films at 65 K.

Figure 2 shows the magnetic $J_c$ as a function of magnetic field. There is a general trend of increased $J_c$ for both 77 K and 65 K where the 65 K plot shows 1% doping having the greatest increase in $J_c$.

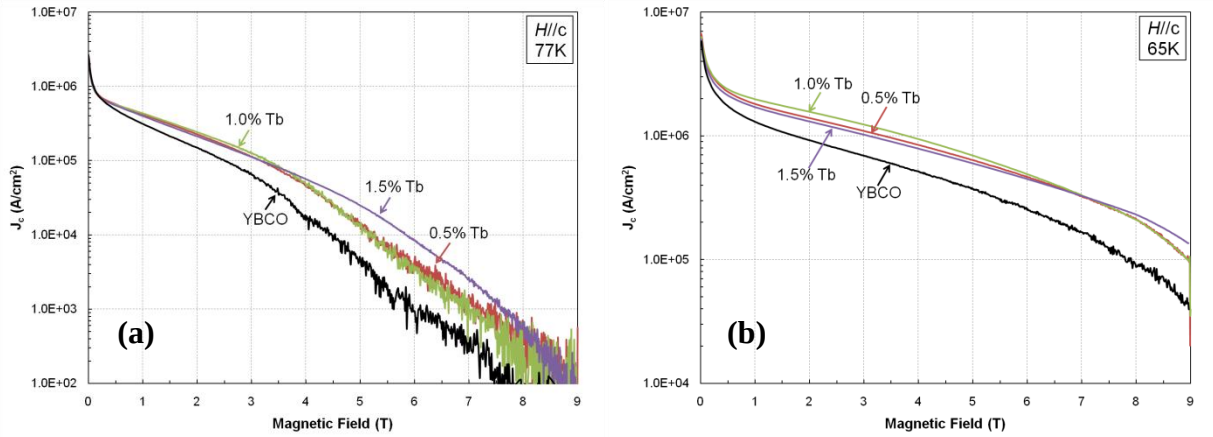


**Figure 2.** (a): $J_c$ for Tb doped films at 77 K, (b): $J_c$ for Tb doped films at 65 K.

The magnetic $F_p$ and $J_c$ plots as a function of magnetic field for Nd doped samples are seen in Figure 3 and 4, respectively. The $F_p$ plots show that all of the concentrations observed of Nd doping increased the pinning forces with 0.75% having the greatest increase out of the observed quantities. These plots show that there is ~1.4x increase in the pinning force maximum at 77 K and ~2x increase in pinning force maximum at 65 K for 0.75% Nd It can be seen in Figure 4.a that at very low magnetic field values there is some degradation of the $J_c$ performance with the minute dopants; however, as seen in the 65 K $J_c$ data found in Figure 4.b the enhancement occurs at all fields. This could imply that additional optimization of the deposition parameters may improve the very low field performance.

It should be noted that upon characterizing the samples it became apparent that at very small levels of dopant additions (e.g. $x < 0.1\%$) there is some inconsistency of the results. This could potentially be due to issues of adding in such minute quantities of dopant and then ensuring a uniform distribution of the small quantity of powder throughout the mixture. In addition to the potential mixing issue these smaller levels of powder are beginning to rival the impurity levels of the starting powder. Even so, the added pinning force due to the deleterious dopants is clearly starting to wane at the lower levels. Further investigation must be taken in order to ensure proper composition of targets and as such we have left the data out for the lowest levels of additions until further study can be done. However, this does not affect the results given here.

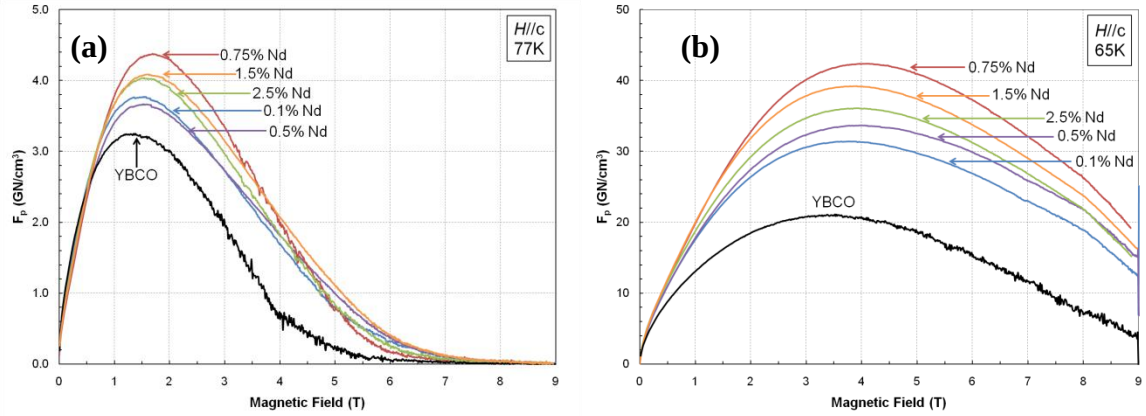


**Figure 3.** (a): Pinning force for neodymium doped films at 77 K, (b): pinning force for neodymium doped films at 65 K.

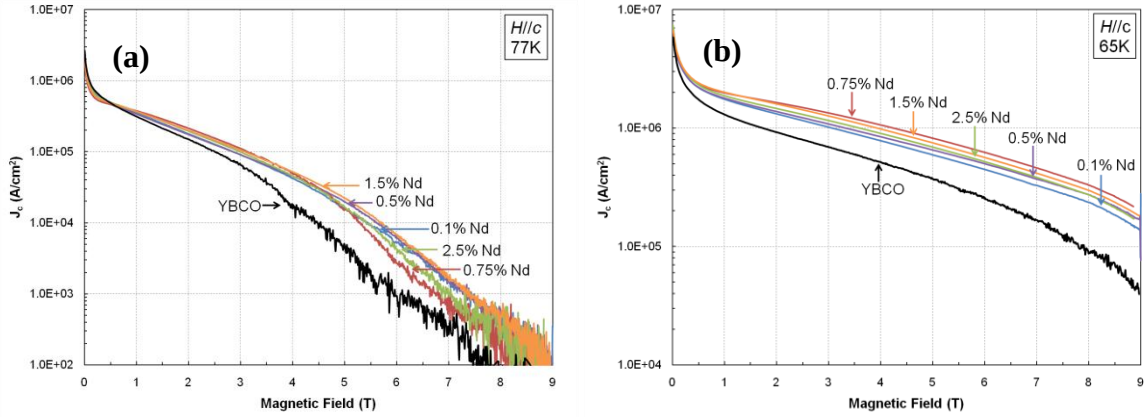


**Figure 4.** (a): $J_c$ for Nd doped films at 77K, (b): $J_c$ for Nd doped films at 65K.

One interesting observation is that the pinning force plots of different concentrations for Nd and Tb increases while maintaining the same relative shape. This could occur from an increase of the pinning force of individual defects, or an increase in overall flux pinning centers. Also, even though the Nd and Tb substitute differently in the $(Y_{1-x}RE_x)BCO$ compound the results show that they optimize similarly. While Tb optimizes around 1.0% over a range of 0.5% to 1.5%, Nd optimizes around 0.75% over a range from 0.5% to 1.5%. Both Nd and Tb have a range of optimization of ~1%. This is very different when large quantities of standard RE dopants are added, further indicating a difference in the minute doping pinning mechanism from standard RE substitution typically used.

Figure 5 shows plots of $J_c$ vs. RE dopant percent molar additions to YBCO for both Nd and Tb at 77 K, 2 T (Figure 5.a) and 65 K, 3 T (Figure 5.b). These plots show that Nd has a range of optimization between 0.5% and 1.5% for both 77 K and 65 K. Tb also optimizes similarly having a range of optimization from 0.5% to 1.5%. Here it can also be seen that for 77 K, 2 T the Tb has very similar $J_c$ values from 0.5% to 1.0%, but at 65 K, 3 T the $J_c$ values of Tb are slightly lower than the Nd. Since there is some spread in the various data points for a given dopant level, one-way Anova statistical analysis was applied to the data set. It supports the finding that the $J_c$s are significantly different as thought.

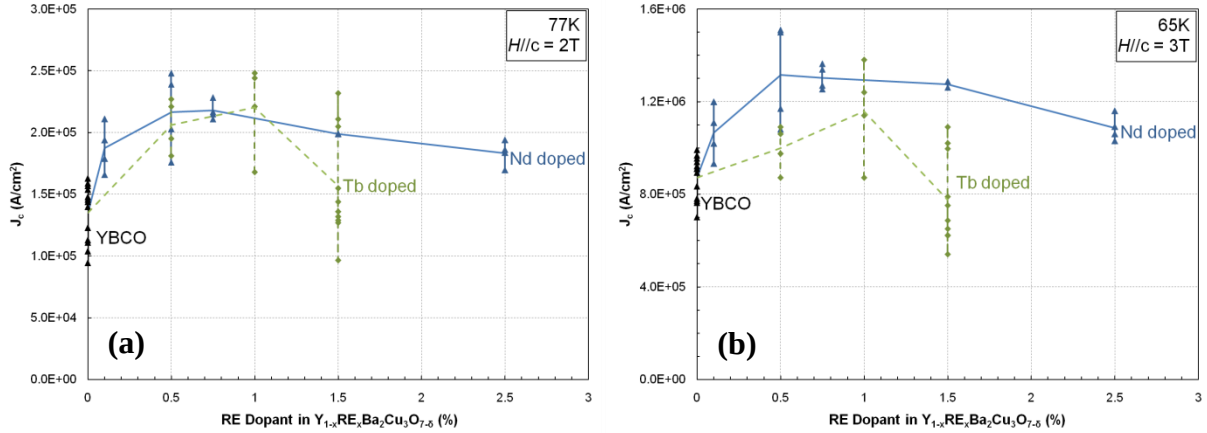


**Figure 5:** $J_c$ vs RE dopant quantity, (a) 77K, 2T (b) 65K, 3T.

The initial analysis of the films microstructure was completed on $(Y_{0.995}Nd_{0.005})BCO$ (Figure 6a) and $(Y_{0.985}Tb_{0.015})BCO$ (figure 6b) using high resolution transmission electron microscope. The images revealed that the Nd doped film had a very straight lattice while the Tb doped film showed significant plane buckling of the YBCO lattice. The Nd film has very fine precipitates having a scale of ~5nm x 1nm of unknown composition. The Tb film only has a very small amount of precipitates having a scale of ~4nm x 10nm in size that are possibly $Y_2O_3$. The precise distributions of both Tb and Nb are not known yet, and further studies are being preformed to verify the dopant locations and consistency of the microstructure. In principle for 1-2 vol% additions and nanoparticle size of 5-7 nm, the matching fields would be on the order of 0.5-2T which is precisely where the pinning force was increased at 77K. So the increase of flux pinning is not unreasonable considering the nanoparticle sizes observed. Nanoparticles were demonstrated to increase flux pinning [1], so we are expecting that a similar mechanism is occurring; e.g. at least for Nd dopants.

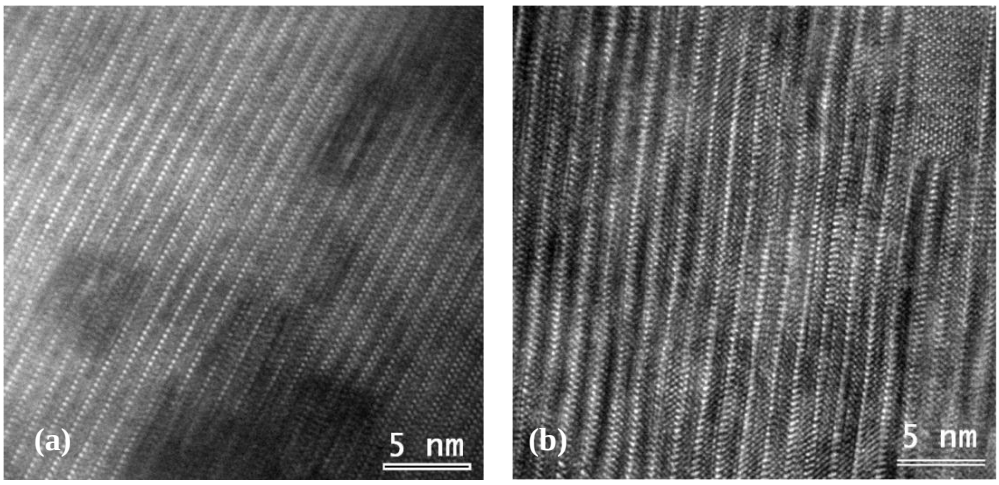

**Figure 6.** Cross-sectional TEM images of (a) $(Y_{0.995}Nd_{0.005})BCO$, (b) $(Y_{0.985}Tb_{0.015})BCO$

## CONCLUSIONS

Nd and Tb minutely doped YBCO targets were created using solid state reaction techniques which were used to produce Nd and Tb minutely doped YBCO films by PLD. The results suggest that when the Nd and Tb dopants were added in very small quantities, they behaved similarly in pinning force enhancement and range of doping optimization, even though both tend to create a defect structure in YBCO via different mechanisms. Both dopants have a 1% range of optimization for ~0.5% to 1.5% molar concentration in $Y_{1-x}RE_xBa_2Cu_3O_{7-\delta}$. The pinning forces at 77 K 2 T were very similar for Nd and Tb, while at 65 K 3 T the Nd doping had slightly increased Jc values across the range of doping. Initial TEM images also reveal that the dopants do incorporate differently into the YBCO while have very similar enhancements in both range and relative optimization concentrations. Work is now in progress to transfer this method of doping to other deposition methods (MOD initially) to demonstrate its ease of incorporation regardless of process.

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